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Migration of ions through silicic acid gels

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A STUDY ON THE MIGRATION OF IONS THROUGH SILICIC ACID GELS

A thesis, presented to the Department of Chemistry at Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry, by

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INTRODUCTION

Ever since Liesegang (1), rediscovered the phenomenon of rhythmic precipitation first due to Runge (2), the colloid chemists have been using their ingenuity in attempts to explain the factors responsible for the formation of Liesegang rings. The theories resulting from such investigation have not been entirely satisfactory. In recent years the problem has been taken up by the students of wave mechanics in hope of conquering that which has so far defied the chemists.

It is hoped that by continuing the work of Bieleski (3) and Rothemich (4) with the probing electrode, one of the many theories concerning the phenomenon will be substantiated or an entirely new theory established.

HISTORICAL

The numerous investigations which have been carried on in connection with the Liesegang phenomenon have been carefully compiled by Hedges (5) in his book entitled, "The Liesegang Phenomenon". This work in turn has been abstracted by Rothermich (4) and may be found in his thesis.

An interesting supposition has recently been published by Wulff and Christiansen (6). They say that, "the effect in question is a macroscopic, quantum mechanic effect". It is clear that the material particles have to perform a very slow motion in diffusion. For such a motion they apply the De Broglie equation:

$$\lambda = \frac{h}{mv}$$

where m is the mass of the moving particle, v the average velocity (not to be confused with the root of the average velocity squared) at the point under consideration. When $m = 100/6 \times 10^{23}$ and $h = 6.55 \times 10^{-27}$, $x \sim 40.10^{-6} \times \frac{1}{v}$.

In other words when v becomes as small as 10^{-3} -- 10^{-5} can, λ becomes macrospically observed. In diffusion velocities are expected to be of the order of magnitude $\sqrt{D/t}$ where D is the diffusion co-efficient and t the time after beginning diffusion. There the D of the order of magnitude is 10^{-5}, one is now able to expect

with a course of minute wave lengths of macroscopic dimensions.

Similar considerations were published first Michaleff, Nikiforoff and Schemjakin (7). The authors mentioned also used De Broglie's equation as a basis for their calculations. They have measured on one hand the average line distance $\overline{\Delta}$. The latter identified with λ. Now the line, however, seems to be a kind of node line, whose distance therefore is half a wave length. Moreover it is shown below that not one, but several wave systems exist alternating with each other. It follows also that $\overline{\Delta} = \lambda/4$. For the mass we must insert the mass of the particle whose motion is being observed, that is, the molecular mass of the precipitated substance. It immediately becomes apparent that

$$\overline{v} \cdot \overline{\Delta} = \overline{v} \cdot \frac{\lambda}{4} = \frac{1}{4} \cdot \frac{h}{m} = \frac{3.94 \times 10^{-3}}{4} \cdot \frac{1}{M}$$

for $Ag_2 Cr_2 O_7$ M is 432 and therefore $\overline{v}\,\overline{\Delta} = 2.28 \times 10^{-6}$ while the above mentioned investigator found 2.26×10^{-6}. Of the other substances investigated the agreement is not so close, but lies, however, in the right order of magnitude.

According to the classical diffusion theory and the experiments of Morse and Pierce the places and times of the precipitating phenomenon are combined by means of the equation. $\frac{x^2}{t} = \text{const.}$

The velocity of the progressive precipitation follows from this,

$$d\,x\,/dt = x/2t$$

On setting this in De Broglie's equation it becomes

$\lambda \cdot x/2t = h/m$ or

$$x^2/t = 2\,x/\lambda \cdot h/m$$

It follows therefore that $\lambda/x = \text{const.}$

The goal of Wulff and Christiansen was to prove numerically the two relations $x^2/t = K_I$ and $\lambda/x = K_2$. Numerous experiments proved, however, that both relations have only a limited validity. Because of this they use only approximate agreements to develop the theory accurately.

Lakhari and Mathur (8) show that

$$\frac{\log xn_I}{\log xn_2} = \sqrt[3]{\frac{C_2}{C_I}}$$

where xn_I and xn_2 are the distances from the gel surface of the nth ring for the silver nitrate solutions C_I and C_2. The above equation being valid within experimental error.

Schemjakin and Nikiforoff (7) show that actually the product of the distance between the precipitated bands, and the migration velocity of the diffusion plane (at the same place) produces a constant magnitude for the given periodic reaction process. They also show that the magnitude of the distances between the precipitation

plane is in direct proportion to the decrease of migration velocity of the diffusion plane in the gel.

Toshiyo Isemura (9) makes use of the equation $\Delta x_n = a + bn + cn^2$ for the ring formation of copper chromate in SiO_2 gel. Δx is equal to the distance between two successive layers and a, b, and c are constants. The equation is found to hold for the above effect.

W. A. Patrick and B. W. Allan (10) have collected data which opposes the Nernst theory of ring formation. Patrick also mentions an electro-kinetic effect which takes place at the surface of the gel and solution, and which is now under investigation.

Jean Ratelade (11) produced ellipses in the form of bands in cellophane under tension. Cellophane was soaked in a .5% solution of potassium bichromate. It was then dried under tension. When thoroughly dry the lower end was suspended in a solution of silver nitrate (8 gms. per 100 C.C.). The ellipses formed were larger the greater the distance from the solution with the major axes normal to the surface of the solution. However, when the direction of tension in the cellophane was parallel to the surface of the solution, the major axes were parallel to the surface of the solution. It

was found that Veil's (12) square root law held for the formation.

CONSTRUCTION

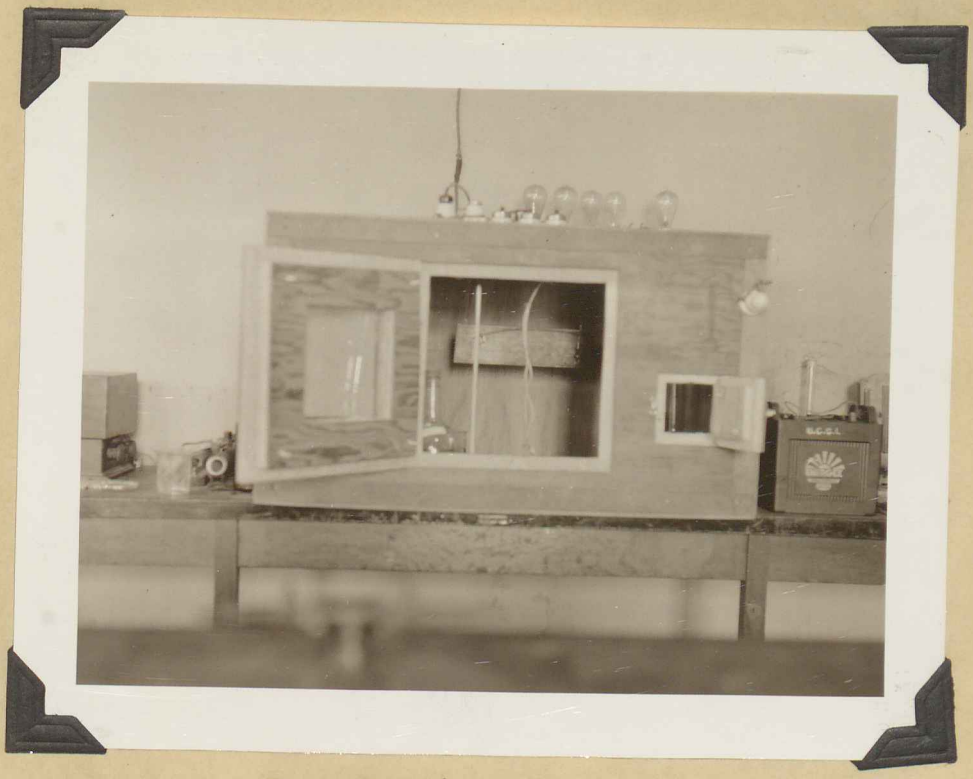
The cell used in this investigation was similar to that used by Fraser (13). It was decided unnecessary to use the cell due to Rothemich, the change in concentration of solution not being great enough to warrant a device to keep it thoroughly stirred.

In constructing the cell proper, two eight-inch test tubes were sealed end on end with a glass tube 10 m.m. in diameter, the tube then being bent into a U shape. A special device was made to hold the tube while holes for the electrodes were drilled. The process of drilling was a tedious one, and much practice was needed before the technique of the operation was thoroughly under control. The drilling was performed with a carballoy drill set with diamonds. Paraffin was poured into the section to be drilled in order to give the glass more body against the pressure of the drill. This paraffin was later melted out, and traces on the sides of the tube removed with benzine. Electrodes were sealed into the tubes with glyptal resin. The electrode areas had to be nearly equal, thus necessitating great care in

the installation. To insure that they extended into the cell the same distance, the cell was set into the drilling device and a smaller tube placed inside the larger tube. The wires were sealed in with their ends resting on the smaller tube. The cell was then mounted on a stand as shown in the photograph.

The cells were extremely fragile due to the strain set up in the glass while drilling. Several cells cracked for no apparent reason. It is suggested that future experimenters construct a muffle furnace and anneal the glass after drilling. One might also try constructing smear holes by means of a "smear seal".

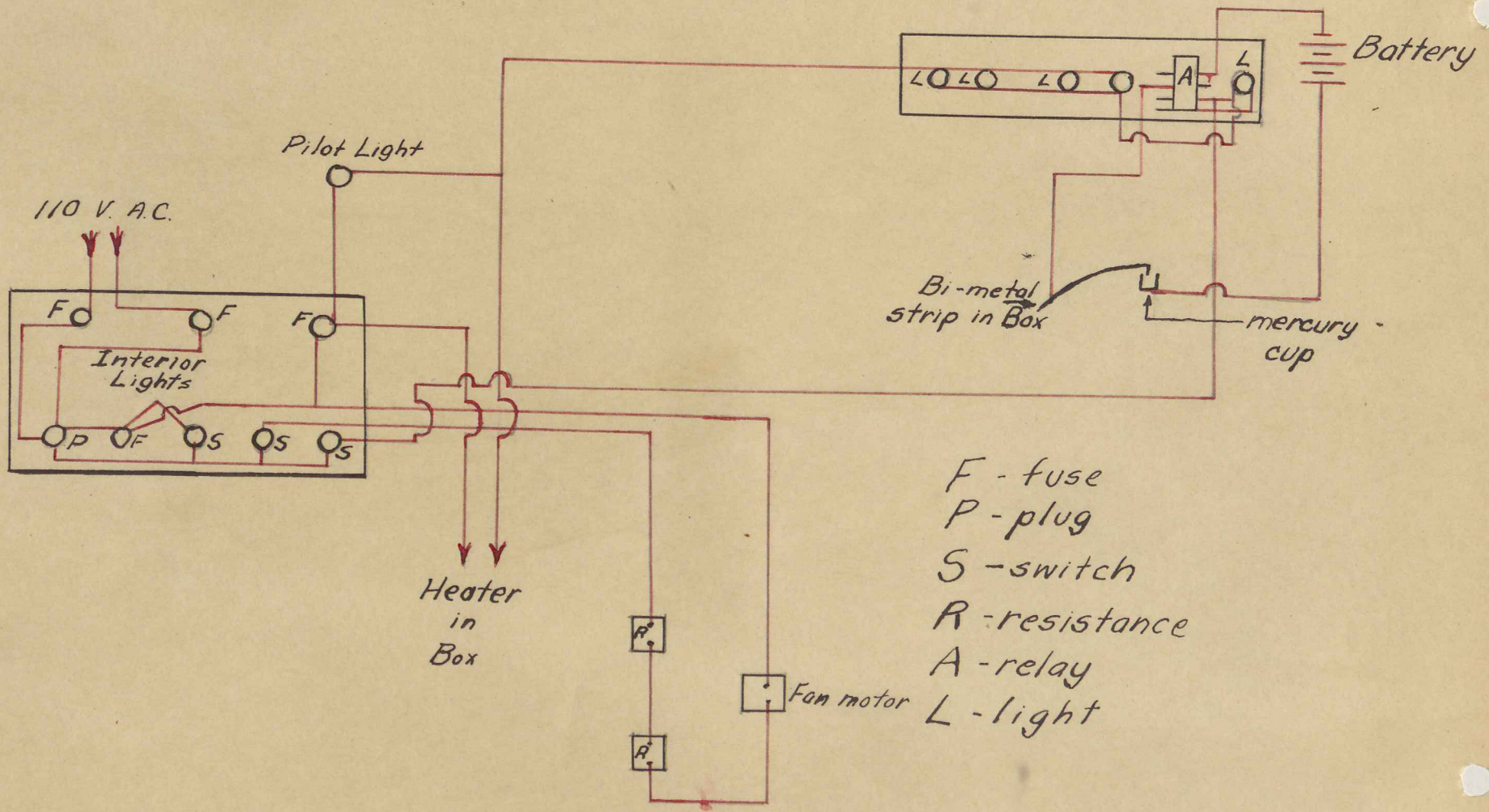
The distance between the electrodes and distance from the gel surface to the first electrode was measured by means of a cathetometer. The diffusion was run at constant temperature, the air bath used being that constructed by Rothemich. The circuit is described in the figure, and the bath itself shown in the photograph.

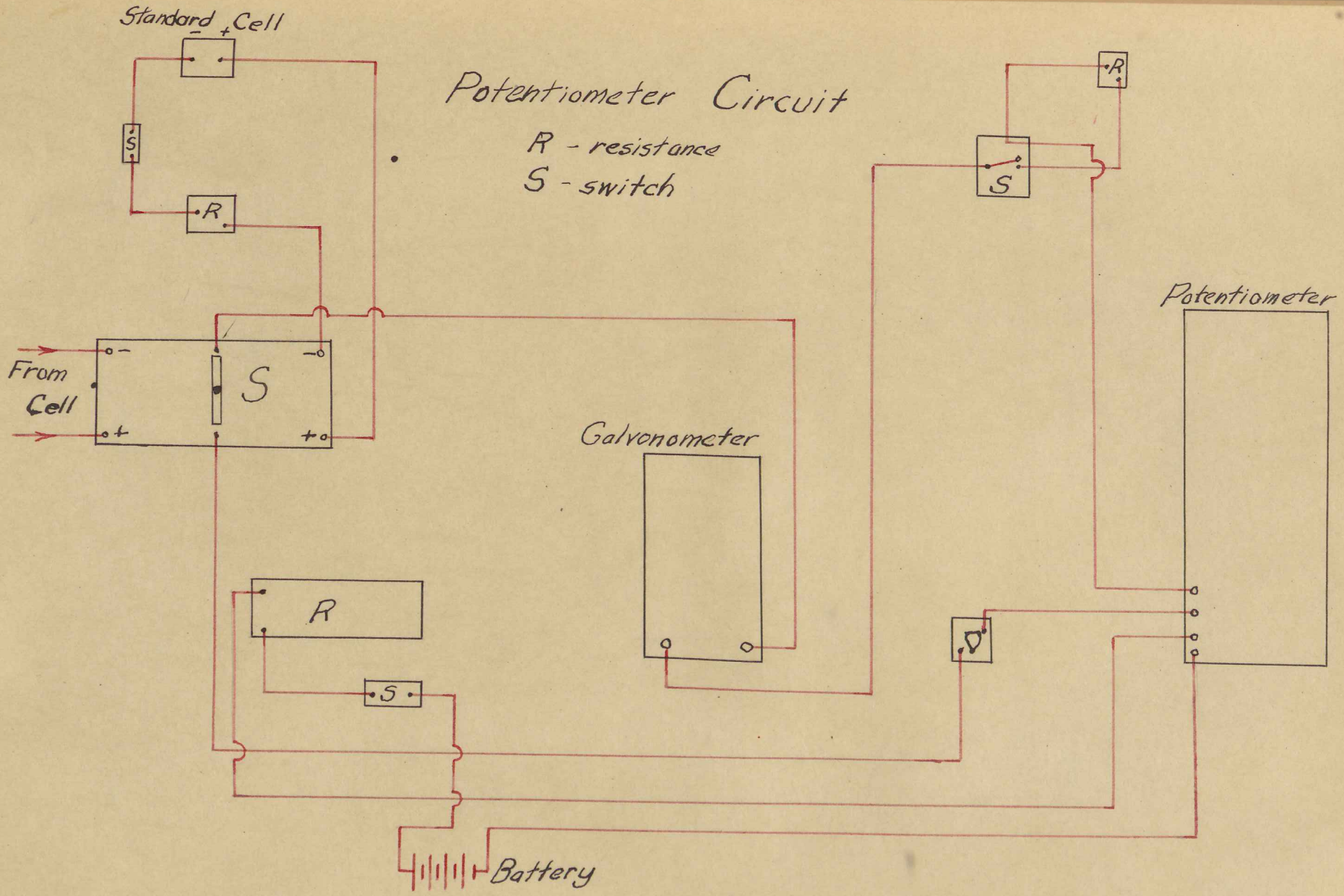


Air - Bath

Cell

Thermostat Connections




Standard Cell
Potentiometer Circuit
R - resistance
S - switch
R
S
R
S
Potentiometer
From Cell
S
Galvonometer
R
S
Battery

PROCEDURE

The cell was erected as shown in the photograph. Copper wires were attached to the lead electrodes for convenience in handling. The cell was washed out with a solution composed of five (5) parts water and one (1) part nitric acid. This procedure was undertaken in order to remove any impurities from the wires. After five (5) minutes the solution was removed, and the cell rinsed thoroughly with distilled water and lead acetate of the concentration to be used in the experiment. If the acid used in washing was too strong or remained in the cell too long, the glyptal resin was attacked and the electrodes loosened.

In order to bring all the electrodes to the same potential they were "short circuited" in .I M lead acetate solution. After a week in this condition the short circuit was removed and the electrodes checked. It was found that the potential difference between the middle reference electrode and the other electrodes was not constant. The shortcircuit was restored and allowed to remain so for another week. The electrodes were again tested. The potential differences had changed, but were not equal or constant. This procedure was continued for

approximately a month before zero potential for all electrodes was reached. However, on placing the gel in the apparatus, they commenced to vary and could not be brought to constancy.

I deem it well to digress for the moment, and mention a few experiments performed to try and determine the cause of the inconstancy of the electrodes.

It was first thought that the drawing and treatment of the lead wire may have been the cause. However, on investigation it was found that the wire had received the same treatment as that used by previous workers. A piece of glyptal resin was then placed in lead acetate to see if the two reacted. Such was not the case, however. Lead wires were then hung on a glass rod; the rod placed across the rim of a beaker with the lead wires dipping into lead acetate solution. Such wires were found to come to zero potential more readily.

An entire new cell was built, and exactly the same procedure undertaken. The electrodes became constant after a period of three weeks and remained so when gel replaced the lead acetate solution. It was with this cell that the run described in this thesis was taken. The diffusing solution was changed every twenty-four hours. A solution of lead acetate of the

same concentration as the lead acetate in the gel was placed on the gel in the reference tube. This too was replenished from time to time as conditions warranted. The diffusion was run at a temperature of 25°C.

TABLE I

Gel mixture - 100 c.c. 1.06 water glass
50 c.c. 2N acetic acid
50 c.c. .04M lead acetate

Resulting gel .01M with respect to lead acetate

Diffusing salt .1M lead acetate

Reference electrode B

Electrode	Distance below surface of gel
1.	.785 cm.
2.	1.685 "
3.	2.750 "
4.	3.665 "
5.	4.600 "
6.	5.570 "
7.	6.495 "
8.	7.515 "
9.	9.535 "
10.	11.465 "

Electrodes

ne		1	2	3	4	5	6	7	8	9	10
		.0005	.0001	.0000	.0001	.0001	.0001	.0001	.0004	.0001	.0005
r.	30min	.0041	.0001	.0001	.0001	.0001	.0001	.0001	.0004	.0001	.0005
r.	12min	.0128	.0002	.0001	.0001	.0000	.0001	.0000	.0004	.0001	.0005
r.	9min	.0170	.0003	.0005	.0001	.0000	.0001	.0000	.0004	.0001	.0005
r.	8min	.0195	.0006	.0003	.0001	.0000	.0001	.0000	.0004	.0000	.0005
r.	25min	.0245	.002	.0001	.0001	.0000	.0001	.0000	.0005	.0000	.0005
r.	17min	.0277	.0034	.0001	.0001	.0000	.0001	.0000	.0005	.0000	.0004
r.	14min	.0300	.005	.0002	.0001	.0000	.0001	.0001	.0005	.0001	.0004
r.	52min	.0320	.0063	.0002	.0001	-.0001	.0001	.0001	.0005	.0001	.0004
r.	20min	.0339	.0085	.0004	.0001	.0001	.0001	.0001	.0005	.0001	.0004
r.	26min	.0355	.0114	.0011	.0001	-.0001	.0002	.0001	.0005	.0001	.0004
r.	24min	.0367	.0135	.0017	.0001	.0001	.0002	.0001	.0005	.0001	.0004
r.	45min	.0385	.0154	.0024	.0002	.0000	.0002	.0001	.0005	.0001	.0004
r.	57min	.0415	.0169	.0034	.0004	-.0005	.0003	.0001	.0005	.0001	.0004
r.	46min	.0427	.0181	.0039	.0005	-.0007	.0003	.0001	.0005	.0001	.0004
r.	48min	.0437	.0194	.0045	.0007	-.001	.0003	.0001	.0005	.0001	.0004
r.	27min	.0449	.0210	.0054	.001	-.0012	.0004	.0001	.0007	.0002	.0004
r.	17min	.0454	.0223	.0059	.0013	-.0013	.0004	.0001	.0007	.0002	.00045
r.	50min	.0459	.0231	.0065	.0015	-.0013	.0004	.0001	.0007	.0002	.00045
r.	34min	.0470	.0245	.0079	.0020	-.0013	.0004	.0001	.0007	.0002	.0004
r.	51min	.0471	.0260	.0086	.0025	-.0013	.0004	.0001	.0007	.0002	.0004
r.	46min	.0478	.0275	.0101	.0030	-.0013	.0005	.0001	.0006	.0003	.0004
r.	56min	.0537	.0363	.0178	.0085	+.001	.0012	.0003	.0004	.0006	.0004
r.	15min	.0564	.0406	.0244	.0133	.0038	.0024	.0005	.0001	.0005	.0003
r.	56min	.0577	.0439	.0286	.0180	.0076	.0041	.0010	-.0004	.0004	.0000
r.	41min	.0580	.0448	.0299	.0190	.0087	.0048	.0012	.0001	.0003	.0000
r.	25min	.0589	.0462	.0319	.0211	.0112	.0060	.0018	-.0004	.0001	-.0003
r.	53min	.0590	.0475	.0343	.0240	.0142	.0080	.0031	-.0005	-.0001	-.0005
r.	46min	.0596	.0489	.0361	.0264	.0160	.0104	.0044	.0000	-.0001	-.001
r.	06min	.0596	.0499	.0376	.0283	.0181	.0121	.0056	.0009	-.0002	-.0014
r.	16min	.0596	.0507	.0400	.0312	.0220	.0151	.0087	.0034	-.0002	-.0020
r.	35min	.0596	.0514	.0410	.0325	.0235	.0168	.0100	.0045	-.0001	-.0023
r.	25min	.0596	.0520	.0419	.0336	.0251	.0185	.0118	.0057	.0001	-.0025
r.	40min	.0598	.0522	.0425	.0344	.0260	.0194	.0128	.0066	.0005	-.0026
r.	24min	.0599	.0528	.0431	.0354	.0273	.0206	.0143	.0078	.0013	-.0025
r.	32min	.0605	.0534	.0437	.0361	.0281	.0216	.0152	.0090	.0018	-.0025

Gel Split

Reference Electrodes

A	C	Time	
.0001	.0003	0	
.0004	.0004	11hr.	14min.
.0005	.0004	13hr.	52min.
.0007	.0004	15hr.	20min.
.0011	.0004	18hr.	26min.
.0014	.0004	21hr.	24min.
.0019	.0004	23hr.	45min.
.0024	.0003	26hr.	57min.
.0029	.0003	30hr.	48min.
.0031		33hr.	27min.
.0036	.0003	35hr.	17min.
.0039	.0003	39hr.	34min.
.0045	.0003	42hr.	51min.
.0049	.0003	46hr.	46min.

A	C	Time	
.0079	.0003	92hr.	56min.
.0084	.0001	93hr.	15min.
.0093	-.0001	118hr.	56min.
.0095	-.0003	125hr.	41min.
.01	-.0005	141hr.	25min.
.0105	-.0009	166hr.	53min.
.011	-.0014	191hr.	46min.
.0115	-.002	215hr.	06min.
.0124	-.0029	238hr.	16min.
.0120	-.0039	262hr.	35min.
.0116	-.0051	290hr.	25min.
.0114	-.0055	310hr.	40min.
.0118	-.0059	337hr.	24min.
.0125	-.0059	358hr.	32min.

GRAPH

In the first table the time of reading is for electrode 1. It was found that about one minute elapsed between readings for each successive electrode. The correct times were recorded, but in graphing no serious error is introduced by using the time tabulated for electrode 1. In the graph time is plotted as abscissal and electromotive force as ordinates. On the ordinate axis two (2) mm. represent .0005 volts. On the abscissa one (1) m.m. represents one hour.

ANALYSIS OF RESULTS.

The cell may be represented by the following diagram.

$$Pb. / Pb. (C_1^{++}) // Pb. (C_o^{++}) / Pb.$$

However, since we do not have a sharp boundary between the Pb. ions about the reference electrodes and the Pb. ions about the electrodes in the experimental tube, this is not strictly true. If we assume that the cell acts as represented the electromotive force is given by:

$E = -\frac{RT}{NF} \ln \frac{a_1}{a_o}$ where 'a' is the activity of the lead ions.

$$E = -\frac{8.316 \text{ volt coulomb/degree } 298 \text{ degrees}}{2 \text{ Faradays } 96540 \text{ coulomb/Faraday}} \ln \frac{a_1}{a_o}$$

$$E = -.0293 \log \frac{a_1}{a_o}$$

The electromotive forces are correct as measured in the table. However, owing to the thermodynarnic convention we must take them as negative in making calculations. Some calculations are recorded in the following table.

TABLE II

Distance from Gel surface	Time in hrs.	E.M.F. in volts	$10^9 \frac{a_1}{a_0}$	$\frac{a_1}{a_0}$
.785	0	0	0	1
	15	.0330	1.126	10.30
	25	.0405	1.382	24.10
	50	.0495	1.689	48.87
	75	.0540	1.843	69.67
	100	.0565	1.928	84.73
maximum	360	.0600	2.047	110.6
1.685 cm.	0	0	0	1
	15	.0085	.2901	1.950
	25	.0155	.5290	3.381
	50	.0290	.9898	9.768
	100	.0420	1.434	27.17
	360	.0535	1.826	67.00
2.750 cm.	0	0	0	1
	25	.0025	.08532	1.217
	100	.0255	.8703	7.418
	150	.0330	1.126	10.30
	200	.0370	1.263	18.32
	360	.0435	1.485	30.55
3.665 cm.	0	0	0	1
	50	.0035	.1196	1.317
	100	.0140	.4778	3.005
	200	.0270	.9215	8.346
	300	.0340	1.161	14.45
	360	.0360	1.229	16.94
4.600 cm.	0	0	0	1
	40	-.0013	-.4437	.3600
	150	.0070	.2389	1.733
	200	.0200	.6826	4.815
	360	.0275	.9386	8.682

It is impossible to calculate the absolute concentration of the lead ions migrating into the gel, because of the lack of information on the activity coefficient of lead ions. It is quite evident, however, that profound changes in the activity must take place in the gel.

EXPERIMENTAL

After the first run had been gotten successfully under way, it was decided that some more satisfactory procedure of procuring like electrodes would have to be found. Silver is obtainable in a much purer form than lead, so it was thought that silver would serve as electrodes in a much better manner.

A cell was constructed in the same manner as previously described only using silver as electrodes. Silver nitrate was then placed in the apparatus and an endeavor made to plate the electrodes using one electrode as cathode and another as anode. This procedure was not at all successful, and the cell was rebuilt with new electrodes. The new electrodes were sandpapered, and handled at all times with paper in order to give them a rough surface and avoid contamination. Some silver acetate was prepared by digesting silver carbonate in acetic acid. The silver acetate was then placed in the cell and the electrodes short circuited.

At this time experiments with gelatin were made in hope of being able to investigate the original Liesegang phenomenon. It was found that a four percent (4%) solution

of gelatin gave the gel best suited for the work. However, when potassium dichromate was diffused into a gel containing silver nitrate, the dichromate oxidized the gelatin if too strong. On the other hand, if a weaker solution was used putrescence set in the gel before enough rings were formed to warrant investigation. Agar gels were next tried, but no rings formed.

When the silver electrodes were tested to find out if they had reached zero potential a rather curious effect was noted. A transient electromotive force appeared when contact was made with the galvanometer key. The voltage thus produced quickly died down to a steady state. A gel was placed in the cell after the electrodes had become alike. On setting, however, the electrodes lost constancy and varied from day to day. It would appear from a cursory examination that the gel had set before the equilibrium of the constituents of the gel had been reached. The cell never did return to the condition it had been in when filled with silver acetate and was discarded. Experiments were run with silver wires dipping into a beaker of silver acetate. The wires did not reach the same potentials, but the variations were not as flagrant as the variations of the wires in the cell.

A cell using copper electrodes was next constructed, the electrodes being installed in the same manner as those of the silver cell described above. Nevertheless the same condition existed as in previous cells. All told two cells were built and neither one reached constancy. This fact, however, may be accounted for in the following manner. A precipitate was noticed on the electrodes after they had been immersed in copper sulphate for a week. This precipitate would not dissolve in water, but did in water slightly acidified with hydrochloric acid. From such tests, it seems that the precipitate was the basic carbonate of copper. The copper sulphate used was carbon dioxide free. Experiments with wires dipping in copper sulphate in beakers were run. The variations occurred there, but were not as great.

The problem as presented here seems to be one of reproducing electrodes. As a matter of fact, I believe we should regard the curves presented herein very lightly in the region of low potentials due to the unstableness of the electrodes. There seems to be nothing definite in the way of reproducing electrodes according to the literature. However, let us consider the work done above. We notice that electrodes in a cell are harder to bring to constancy than those in a beaker. Of course,

the wires in the cell are subject to heat while being sealed in. From this fact we should gather that the less handling the better the results should be. We might also conclude from above that we should use electrodes made only of the softer metals.

I deem it proper at this time to offer a few suggestions for future work. On turning to the table entitled, "Reference Electrodes", it is seen that a migration, although very small, has occurred (it might be worth while to investigate this phenomenon). In order to prevent such a migration on a similar run, one might cover the surface with oil. This would keep air away from the gel and would contain no material capable of effecting a change in E.M.F. The time spent in constructing cells might easily be cut down by making "smear seals" instead of drilling holes.

CONCLUSION

Proof and disproof of theories in chemical research are the inspirations that impel to new theories, the proof or disproof of which, in turn, comprise the mileposts of progress. Although a new theory has not been advanced, or an old one substantiated, the field of work has been narrowed down, and some of the pitfalls marked for the next investigator. It is hoped that this thesis may represent at least a few modest steps toward the solution of this problem.

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